Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2012.749365

51 (2013) 3463–3471
April

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Removing Cd^{2+} from water and wastewater by blowy sand; the effects of total hardness and pH

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Received 16 March 2012; Accepted 25 July 2012

ABSTRACT

In the present work, blowy sand, as a cheap and available adsorbent, was employed to remove the Cd^{2+} from water and obtain the best kinetic and isotherm models for this elimination process. In addition, the effects of total hardness and pH on this process were examined to obtain the best conditions for elimination of Cd^{2+}. The calibration of kinetic and isotherm models shows that the model presented by Ho and co-workers is the best kinetic model and Redlich–Peterson model is the best isotherm model for presentation of our results. The pH equal to 5 is the best acidic condition to remove Cd^{2+} in all conditions. Moreover, by the increase of total hardness from 0 to 320 (in milligrams of calcium carbonate), the efficiency and capacity of adsorption will decrease, respectively, from 80.4% to 18.7% and from 0.331 to 0.067 mg/g. The reusability of adsorbent without decreasing its efficiency is three times.

Keywords: Cadmium; Blowy sand; Water hardness; Isotherm; Kinetic

1. Introduction

Propagation of heavy metals in air, water, soil, and other environments is one of the most important problems in all countries [1]. These metals have commonly toxic effect on human's (and animal's) body and they cannot be decomposed to the safe materials. The main source of these metals is industrial sewage [2,3]. In countries with dry climate, home and industrial sewages can be used for irrigation of farms. Therefore, it is important to eliminate toxic materials from wastewaters and prepare high quality water to irrigate the farms.

Because of the importance of eliminating toxic materials, many studies have been done on the characteristics, kinetic, equilibrium, and elimination of various heavy metals and other toxic materials [4–19]. Cadmium, as an important member of toxic heavy metals, has harmful effects on the health of animals and humans [20]. Since cadmium is a very important material in plating, solder, and electric industry, it can be usually found in water. Cadmium is entered into the body through food and water [21] and the maximum cadmium allowed in drinking water is 5 μg/L [22]. To remove cadmium from water resources, different adsorbents like clay [23], riverbed sand [24], cellulose acetate [25], olive cake [26], nanotubes [27], beach sand [28], polyphenols (extracted from tea) [29], activated carbon [30], modified silica [31], soil [32], bread's yeast [33], seaweed [34], and the leaf of *Platanus orientalis* [35] have been used and the results are reported in the literature. Despite the large number

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1944-3994/1944-3986

of employed adsorbents for cadmium removal, research in this area still continues to find more efficient, available and cheaper adsorbents. Therefore, discovering new materials for the adsorption of toxic materials is very important and their efficiencies in the removal process should be also worked out clearly.

In this work, we employed blowy sand of Sistan's plain for this purpose. This is a cheap material and available in large scale. So that, we have tried full attempt to explore the use of blowy sand of Sistan's plain for elimination of Cd^{2+} from water. In our research, the effects of total hardness and pH on this removal process were examined to obtain the best conditions. Moreover, kinetic and isotherm models and the optimum amounts for pH and total hardness [36] have been investigated in our study. Details of our experiments and the results obtained in this work are presented below.

2. Material and methods

2.1. General method and instrumentation

The solutions of Cd^{2+} were prepared from standard solution, bought from Merck Company (99.9%), and distilled water. Our adsorbent were collected from the Sistan's plain by hand and then separated by size. The sand with the sizes between 125 and 150 μm were used in our experiments. For each experiment, 250 mg of sieved adsorbent was poured into the 250 mL of distilled water and shaken for 2 h in 150 rounds per minute (rpm) speed. Then the adsorbent was separated by simple filtration, dried in oven at 110°C for 24 h [24] and reused. The water samples were kept in nylon bags for future analyses. We used Cd^{2+} solution with 5 mg/L concentration because this amount is normal quantity for natural samples. Statistical processing our data was carried out using Matlab software version 7.8.0.347. To determine the amount of Cd^{2+}, Merck Spectroquant instrument was used and to determine the pH, PTR-79 was employed.

2.2. Preparation of water samples

Water sample with total hardness equal to 0, 40, 100, 200, and 320 mg/L (in mg $CaCO_3$) was prepared from distilled water and $CaCl_2$ (99%) and $MgCl_2$ (98%, obtained from Merck) and then the appropriate amount of Cd^{2+} solution was added. The total hardness (TH) was calculated from the equation presented by Weiner [37] as below:

$$\mathrm{TH} = 2.5[\mathrm{Ca}^{2+}] + 4.12[\mathrm{Mg}^{2+}]$$

where cations concentration in mg/L.

The TH of each sample was exactly determined by titration with standard EDTA solution.

2.3. Batch experiments

In batch experiments, 50 mL of sample solution were poured into a 250 mL beaker that previously washed first with nitric acid (1M) and then with distilled water. All solutions first filtered by filtration paper No. 40. The pH of samples was determined by PTR 79 pH meter and adsorption experiments were done using Merck Spectroquant. To obtain the concentration of Cd^{2+}, the calibration curve was obtained from the absorption of standard Cd^{2+} solutions (0, 2, 4, 6, 8, and 10 mg/L Cd^{2+} in distilled water) and then the concentration of Cd^{2+} samples were obtained from this curve. All adsorptions were carried out at room temperature. The temperatures of all experiment were fixed at 24°C by water bath.

2.4. Optimization of pH

For each sample, 0.5 g adsorbent was poured into 250 mL beaker and the solution of Cd^{2+} (5 mg/L) was added to the vessel [24]. Six different solutions with pH equal to 3, 4, 5, 6, 7, and 8 were prepared from standard buffers and used for fixing the pH of each sample. Each sample was shaken for 5 min at 100 rpm at 24°C and then used for further analysis.

2.5. Presentation of kinetic and isotherm models

For determination of the best kinetic and isotherm models, some models were used that will be introduced in this section (Table 1).

In equations related to kinetic models (Table 1), q_e is the concentration of material adsorbed on the surface of adsorbent (in mg/g), k_f is the adsorption rate constant for Lagergren model (in 1/h), k_s is the adsorption rate constant for Ho and co-workers model (in $\mathrm{mg/L})^{1/n}\mathrm{s})$, k_{AV} is the adsorption rate constant for Avrami model (in 1/h), and n_{AV} is adsorption mechanism factor. In isotherm models, C_{eq} is the concentration at equilibrium in liquid phase (in mg/L), m is the amount of adsorbent (in g/L), k_F is adsorption intensity constant for Freundlich model, n_F is adsorption capacity constant, q_{max} is saturation capacity (in mg/g), K_L (in g/mg) is Langmuir constant, and K_s, n_s, K_r, a_r, and b_r are coefficients of related equations.

In addition to determination of correlation coefficient (R^2), the root mean squares (*RMSE*), mean bias error (*MBE*), and mean of average error (*MAE*) were

Table 1
Common kinetic and isotherm models used in this study

Kinetic models [41]		Isotherm models [62]	
Name	Equation	Name	Equation
Avrami	$q_t = q_e \cdot \{1 - \exp[-(k_{AV} \cdot t)]^{n_{AV}}\}$	Freundlich	$q_{eq} = \frac{x}{m} = k_F C_{eq}^{1/n_F}$
Lagergren	$q_t = q_e \cdot [1 - \exp(-k_f \cdot t)]$	Langmuir	$q_{eq} = \frac{q_{\max} * K_L * C_{eq}}{1 + K_L * C_{eq}}$
Ho and co-workers	$q_t = \frac{k_s \cdot q_e^2 \cdot t}{1 + q_e \cdot k_s \cdot t}$	Sips	$q_{eq} = \frac{q_{\max} * K_L * C_e^{1/n_5}}{1 + K_L * C_e^{1/n_5}}$
		Redlich–Peterson	$Q_{eq} = \frac{K_r * C_{eq}}{1 + a_r * C_{eq}^{br}}$

used to evaluate our models. The equations presenting these values are shown in Table 2. By increasing R^2 and decreasing the other values, the precision of model will be increased and this model can be selected for our experiments.

2.6. Determination of adsorbent specifications

The general specifications of our adsorbent like its chemical properties, specific surface area, and composition were characterized by standard method. We have selected the sands with crystal size between 125 and 150 μm using special sieves and used these sizes in all experiments.

2.6.1. Determination of bonding properties

Fourier transform infrared spectra of compounds were recorded in the 4000–400 cm^{-1} region with BRUKER IFS-66V spectrometer to obtain the bonding and structural properties of adsorbent. Its FT-IR spectra showed some absorption signals in 460–780 cm^{-1} for Al–O and P–O bonds, in 1082 cm^{-1} for Si–O bonds, in 1200–1250 cm^{-1} for C–O bonds, and in 3200–3600 cm^{-1} for O–H bonds.

2.6.2. Determination of specific surface area

To obtain the specific area of adsorbent, we used the adsorption of methylene blue method using Merck Spectroquant instrument. We first prepared calibration curve for this method by determination of concentration of four standard methylene blue solutions (1, 5, 10, 15, and 20 mg/L methylene blue in distilled water) at 600 nm. Then, 1 g of adsorbent was poured into the 17.6 mg/L solution of methylene blue and shakes them in 150 rpm for 1 h. Then the mixture was centrifuged for 5 min at 3600 rpm to deposit the adsorbent. The solution was filtered and its absorption at 600 nm (for methylene blue) was determined. The special area of adsorbent is equal to 11.8 m^2/g using the below equation:

$$S_{MB} = \frac{N_g \times \alpha_{MB} \times N \times 10^{-20}}{M}$$

In the above equation, S_{MB} is the special area in m^2/g, N_g is the number of methylene blue molecules existed on the surface of adsorbent, α_{MB} is the area occupied by methylene blue (obtained: 197.2 Å^2), N is Avogadro's number (6.022×10^{23} 1/mol), and M is the molecular weight of methylene blue (373.9 g/mol).

2.6.3. Determination of chemical composition

The chemical composition of the adsorbent was obtained from the mineral methods reported previously by another Iranian scientists (Farahi et al., it reported in Persian language) and its composition (in w/w percent) was found to be as: quartz (64.3%), calcite (8.1%), clay (4.6%), ortose (3.9%), biotite (3.6%), gypsum (3.4%), absidine (3.0%), muscovite (2.2%), ortoclaz (1.4%), and chlorite (0.9%).

3. Results and discussion

3.1. Optimization of pH

The experiments related to this section were performed with water solutions with five different total hardness (TH = 0, 40, 100, 200, and 320 in mg/L $CaCO_3$) and six different pH (pH = 3, 4, 5, 6, 7, and 8). The results related to the effect of pH on adsorption efficiency in solutions with different total hardness are shown in Fig. 1.

The data presented in the above figure show that the maximum accessible adsorption quantity in different conditions is 80.4%. By the increase of total hardness, the adsorption efficiency decreases. The maximum adsorption for solutions with total hardness equal to 40, 100, 200, and 320 is, respectively, 51.5, 35.9, 28.5, and 18.7%. The slope of diagram related to reduction of adsorption efficiency increases by decreasing total hardness. In other words, increasing the slope of adsorption in $2 < \mathrm{pH} < 5$ is more than decreasing it in pH after 5. This observation can be explained by two reasons. First, in more acidic media ($2 < \mathrm{pH} < 5$), the high concentration of H^+ ion competes with Cd^{2+} for adsorption. Second, for each metal cation, there is a critical area with maximum adsorption efficiency [38] and after this area, the efficiency of adsorption will be decreased. These results are in agreement with previous reports [39].

3.2. The kinetic and equilibrium of adsorption

In this part of our study, the effect of adsorption time on adsorption efficiency is introduced. Fig. 2 presents the results of this study about the relations between total hardness, adsorption time, and adsorption capacity (q_e).

The variation of total hardness has no important effect on the time of equilibrium. In all experiments, the maximum adsorption capacities were obtained during 60 min and after this time, the adsorption capacity decreases by the increase of total hardness. The competition between adsorption of Cd^{2+} and Ca^{2+} or Mg^{2+} is the reason of this observation [40]. In addition, by the increase of total hardness from 40 to 320, the adsorption capacity decreases from 0.21 to 0.073 (in mg Cd/mg adsorbent, briefly mg/g). The maximum adsorption capacity that can be obtained from distilled water is equal to 0.339 mg/g at equilibrium time (60 min).

Another important aspect of this experiment is the higher adsorption rate at initial times. Namely, 78% of adsorption capacity was obtained during first 5 min. In other words, if we do not need the high adsorption capacity, we can obtain good results in very short time (5 min).

3.3. Evaluation of kinetic models

Presentation of kinetic models for adsorption is very important because it provides useful evidences to determinate adsorption mechanism [41,42]. In this work, three kinetic models presented by Aurami, Lagergren and Ho and co-workers (Table 1) were studied to find the best model matched to our experiments. In these experiments, distilled water was used as a main solution and measured the adsorption capacity. The results of these experiments are shown in Fig. 3 and the comparison between important characteristics of different models is listed in Table 3.

As it can be seen from the above table, all three models can be useful, but the model presented by Ho and co-workers has the largest correlation coefficient and the nearest estimated value for q_e (0.338 mg/g) to our experiment (0.339 mg/g). Therefore, we have been selected this model to evaluate our kinetic data for our experiments.

3.4. Isotherm experiments

The effect of total hardness on adsorption capacity was determined in the next part of our study and the results are shown in Fig. 4. These studies show that adsorption capacity and total hardness have inverse relation. In other words, these cations compete with Cd^{2+} for active sites of the adsorbent [43–47].

As it shown in Fig. 4, maximum adsorption capacities equal to 0.331, 0.207, 0.127, 0.115, and 0.067 were obtained, respectively, for solutions with total hardness equal to 0, 40, 100, 200, and 320 mg/L.

3.5. Evaluation of isotherm models

In the last part of this work, different isotherm models have been evaluated to select the best model for our experiments. The results of these evaluations for Freundlich, Redlich–Peterson, Sips, and Langmuir models are shown in Fig. 5 and important characteristics data for these models are listed in Table 4.

According to Fig. 5, all models have nearly the same and have coincident diagrams. However, Freundlich, Redlich–Peterson, and Sips models can describe our experimental data and all of them have the higher correlation coefficient ($R^2 = 0.968$) than Langmuir model. By considering all of our evaluated data, we selected the Redlich–Peterson model for our

Table 2
Important parameters used for evaluation of kinetic and isotherm models

1	$R^2 = 1 - \frac{ESS}{TSS}$	3	$MBE = \frac{\sum_{i=1}^{n}(Z^*(x_i) - Z(x_i))}{n}$
2	$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\{Z^*(x_i) - Z(x_i)\}^2}$	4	$MAE = \frac{\sum_{i=1}^{n}\lvert(Z^*(x_i) - Z(x_i))\rvert}{n}$

TSS = the sum of total squares, *ESS* = the sum of extended squares, n = number of data, $Z^*(x_i)$ = the values obtained from experiment and $Z(x_i)$ = the values obtained from model.

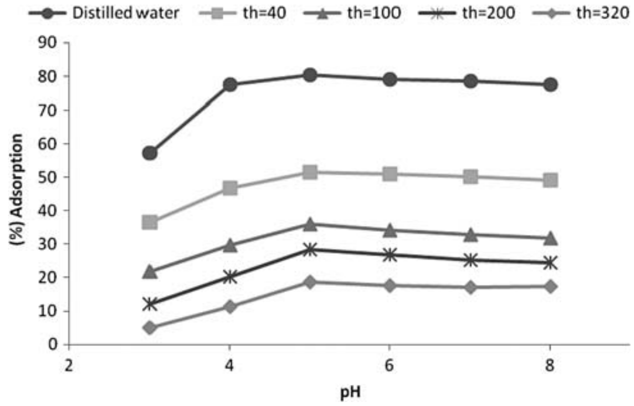

Fig. 1. The effect of pH on adsorption in solutions with different total hardness.

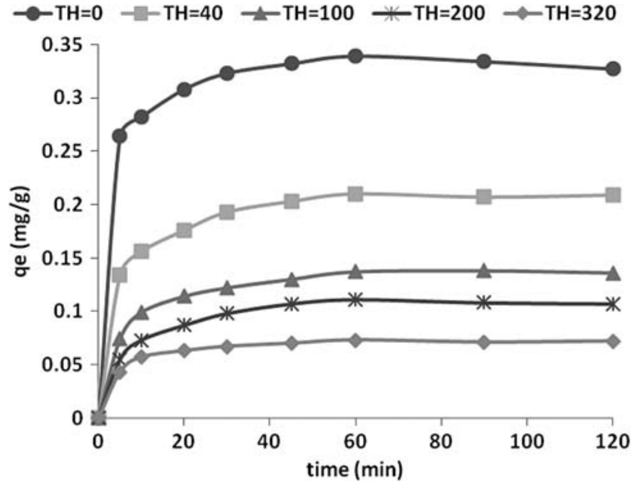

Fig. 2. The effect of total hardness on the time and capacity of adsorption (q_e).

isotherm experiments because it has the lowest doses for *MBE, RMSE,* and *MAE* among all models.

3.6. *The effects of adsorbent amount and initial Cd^{2+} concentration*

It is necessary to determine the effect of adsorbent amount and initial Cd^{2+} concentration to use the optimum values in the other experiments. The effects of adsorption amount on the capacity and efficiency of adsorption are shown, respectively, in Figs. 6 and 7.

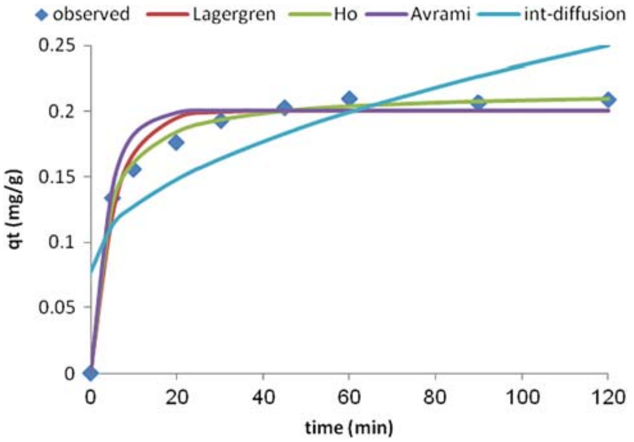

Fig. 3. Comparison between the evaluations of results by different kinetic models in distilled water (th = 0).

According to Figs. 6 and 7, our experiments show that by the increase of the adsorption amount, the adsorbent capacity decreases and adsorption efficiency increases. These results are expectable because addition of adsorbent amount with fixed amount of Cd^{2+} cause decreasing capacity of adsorbent and the total adsorption will be increased. The optimum value for the ratio of adsorbent to water, according to Fig. 7, is 1 mg/mL.

In the next experiment, the effect of initial amount of Cd^{2+} (and also contact time) on the adsorption experiment and the results are shown in Fig. 8. This experiment confirms that by the increase of contact time more than 5 min, no important increase in the adsorption will be observed. Moreover, whatever the initial amount of Cd^{2+} will be less, the adsorption will be more effective and the most effective experiment was observed with 2.5 mg/L initial concentration of Cd^{2+}. However, as we discussed before, the normal concentration of Cd^{2+} in common samples is 5 mg/L and we used this value in our experiments.

Table 3
The comparison between important characteristics of different kinetic models to select the best model (our experimental value for q_e is 0.339)

Model	*MBE*	*RMSE*	*MAE*	R^2	q_e	k^*	Rank
Ho and co-workers	1.45×10^{-4}	6.20×10^{-3}	5.1×10^{-3}	0.996	0.338	1.87	1
Avrami	-1.9×10^{-4}	1.26×10^{-2}	9.9×10^{-3}	0.984	0.325	−0.456	2
Lagergren	-1.60×10^{-4}	1.26×10^{-2}	9.9×10^{-3}	0.984	0.325	0.30	3

k: it is k_s for Ho and co-workers, k_f for Lagergren and k_{AV} for Avrami model.

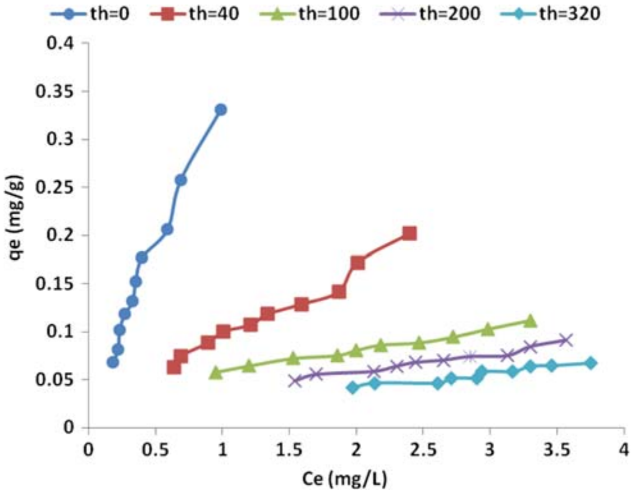

Fig. 4. The effect of total hardness on adsorption capacity at equilibrium (Ce: concentration at equilibrium).

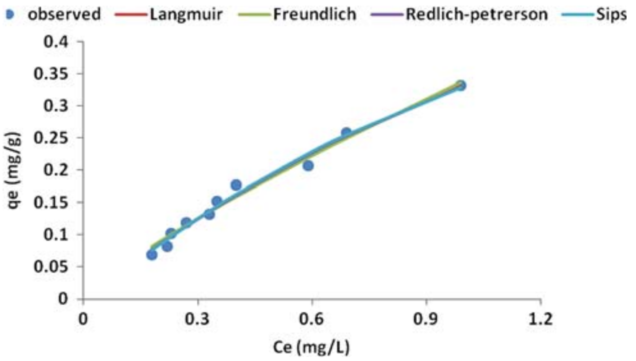

Fig. 5. Comparison between the evaluations of results by different isotherm models in distilled water (th = 0).

3.7. Comparison with previously reported experiments

At this final section, we decide to compare the efficiency, capacity, and other adsorption parameters of our presented work with previously reported works about the elimination of Cd^{2+} from water using various adsorbent. The full results of this comparison are listed in Table 5.

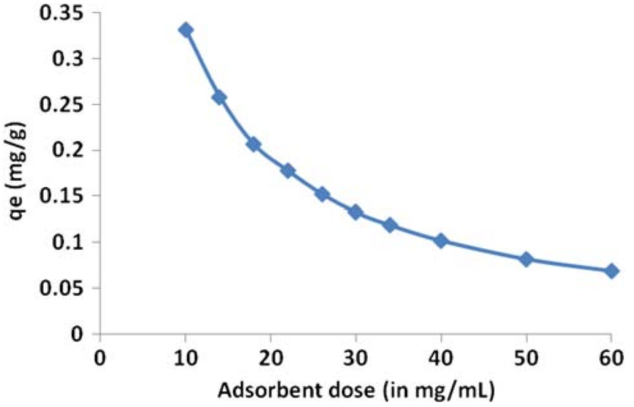

Fig. 6. The effect of adsorption amount on the capacity of adsorption.

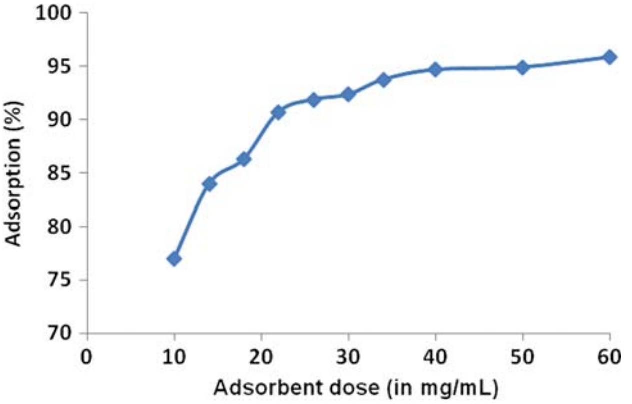

Fig. 7. The effect of adsorption amount on the efficiency of adsorption.

4. Conclusions

In this study, we have introduced the blowy sand as a cheap, available, and useful adsorbent for adsorption of Cd^{2+} from water samples with different total hardness and in different pH. Our experiment

Table 4
The comparison between important characteristics of different isotherm models to select the best model

Model	*MBE*	*RMSE*	*MAE*	R^2	q_{max}	*n* or *a*[a]	*K*[b]	Rank
Freundlich	-1.56×10^{-3}	8.8×10^{-3}	7.5×10^{-3}	0.968	–	0.318	0.74	1
Redlich–Peterson	-1.53×10^{-3}	8.7×10^{-3}	7.4×10^{-3}	0.968	–	1872	597.2	2
Sips	-1.20×10^{-3}	9.1×10^{-3}	7.5×10^{-3}	0.968	8.61	0.73	0.038	3
Langmuir	5.50×10^{-3}	2.2×10^{-2}	1.7×10^{-2}	0.900	97.0	–	0.0029	4

[a] *K* is K_L for Langmuir, K_F for Freundlich, K_s for Sips and K_r for Redlich–Peterson model.

[b] This column refers to n_F for Freundlich, n_s for Sips and a_r for Redlich–Peterson model.

demonstrated that the best kinetic model is Ho and co-workers model and the best isotherm model is Redlich–Peterson model for evaluation of our data. Moreover, by increasing total hardness of water sample, adsorption capacity and adsorption efficiency will decrease because Ca^{2+} and Mg^{2+} ions have competitive effect with Cd^{2+} to occupy the active sites of adsorbent. This decreasing in lower amounts of total hardness is more than that in higher ones. Therefore, to obtain the maximum efficiency for elimination of Cd^{2+} from water samples, reducing total hardness of water is necessary. Moreover, the maximum adsorption of Cd^{2+} by blowy sand was obtained in pH = 5 and during 60 min, increasing pH or the time of adsorption has negative effect on the adsorption efficiency.

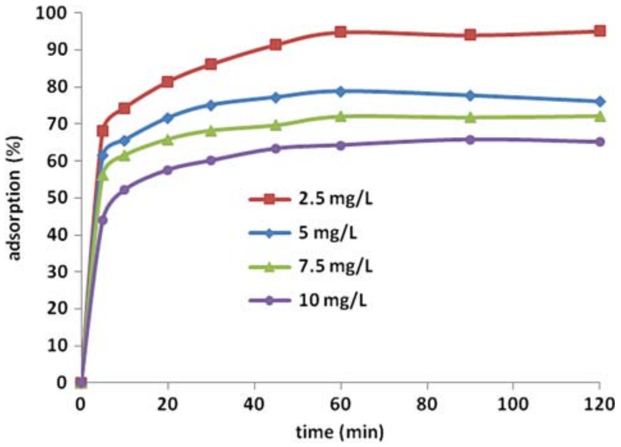

Fig. 8. The Effect of initial Cd^{2+} concentration and contact time and initial concentration on the efficiency of adsorption.

Table 5
Comparison between adsorption parameters for different adsorbent. All values refer to the best and optimum results obtained in the work

Adsorbent	Initial Cd^{2+} concentration (mg/L)	Contact (equilibrium) time (min)	% Adsorption (efficiency)	Adsorption capacity (mg/g)	pH	Reference number
Present work	5	5	80	0.331	5	–
perlite	1	300	55	N.R.[a]	6	[59]
A. bisporus	1	300	68	2.08	6	[60]
L. edodes	1	60	45	716/0	5	[60]
Activated and sulfated carbon	50	N.R.[a]	98.8	N.R.[a]	6	[61]
Bagasse fly ash	14	60	99.9	N.R.[a]	6.5	[48]
Rice chaff	N.R.[a]	120	99	122	7	[35]
Fontinalis antipyretica	N.R.[a]	N.R.[a]	N.R.[a]	28	5	[49]
Vermiculite clay	N.R.[a]	N.R.[a]	N.R.[a]	0.5	N.R.[a]	[50]
Orange waste	N.R.[a]	N.R.[a]	66	0.43	6	[4]
Olive	N.R.[a]	N.R.[a]	N.R.[a]	65.4	6	[26]
Phosphogypsum	N.R.[a]	N.R.[a]	N.R.[a]	131.58	9.5	[5]
Dead Seaweed	2.5	180	90	80	5	[34]
Activated carbon and sulfur	N.R.[a]	N.R.[a]	N.R.[a]	142.86	N.R.[a]	[51]
Anthracite	180	70	N.R.[a]	2	10	[52]
Bio filter	1.9	90	N.R.[a]	0.5	8	[53]
Granular activated carbon	3.4	240	N.R.[a]	0.2	8	[53]
Coconut	N.R.[a]	90	N.R.[a]	0.027	6	[54]
Olive leaf	10	120	98	2.6	6	[55]
Fucus spiralis	10	60	76.6	64	6.5	[56]
Calcite	150	10	99.8	18.52	5	[57]
Carbon nanotube	4	N.R.[a]	N.R.[a]	11	5.5	[45]
Rose leaf	N.R.[a]	10	60	1.16	4	[58]
Virgin	N.R.[a]	90	N.R.[a]	N.R.[a]	6	[11]

[a] No reported.

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